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TRANSPORT PROPERTIES OF CONDUCTIVE POLYMERS

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FINAL REPORT FOR THE PERIOD
August 1, 1986 through September 30, 1987

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J.A. Walker
Principal Investigator

OCTOBER 1987

Rockwell International
Science Center

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A series of free standing films of doped polypyrrole were prepared and characterized by infrared spectroscopic methods. The frequency dependence of the infrared reflectivity of the polymer films was fit to the Drude model for the dielectric function an electron gas. In order to adequately model the observed reflectance spectra, an additional oscillator term was added to the dielectric function to account for electronic transitions that involve mid gap electronic states. Approximate values for the plasma resonance frequency for these materials range between $1-4 \times 10^{-15}/s$, while values for the carrier scattering time were on the order of 10^{-15} s. The spectral analysis also allowed for the calculation of the complex dielectric constants. These constants appared to scale with the dc conductivity of the polymer film. It is suggested that the very short carrier scattering time in conducting polymers limits the observed conductivity and that improvements in conducting polymer synthesis and processing techniques will ultimately result in much higher conductivity levels.

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TABLE OF CONTENTS

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LIST OF FIGURES

LIST OF FIGURES

LIST OF TABLES

FOREWORD

This document is the final report for Contract N00014-86-C-0447, which was carried out between August 1, 1986 and September 30, 1987. The effort was funded by the Office of Naval Research in Arlington, Virginia and was monitored by Dr. Donald Polk.

SUMMARY

The objective of this research was to characterize the electronic transport properties of conducting polymers using optical spectroscopy. The determination of properties such as the carrier lifetime and the plasma resonance frequency are important to the understanding of basic processes in conducting polymers and at the same time yield values for the complex dielectric constants of these materials at infrared frequencies.

Room temperature infrared reflectance spectra have been obtained for a series of electrodeposited films of polypyrrole which were made using different synthesis conditions and incorporated different dopant ions. In general, the reflectivity of the polymer films increases with increasing wavelength between 2.5 and 12.5 microns and then appears to reach a constant magnitude. The magnitude of the far-infrared reflectivity scales with the polymer's dc conductivity.

Room temperature infrared transmission spectra have also been obtained on samples of doped polypyrrole dispersed in potassium bromide. In addition to the absorption bands expected to arise from the polymer backbone and dopant vibrations, these spectra also exhibited broad absorption bands in the near infrared spectral region. Typical transmission spectra were characterized by intense absorption in the near-infrared spectra region (2.5 to 5 microns). The transmission then increases wavelength. The near-IR absorption also appears to scale with the polymer's conductivity.

Approximate values of the plasma resonance and carrier lifetime could be obtained from a Drude-type analysis of the reflectance curves. In order to adequately model the infrared reflectivity, however, a second oscillator term was added to the dielectric function to account for bipolaronic band gap transitions.[1] The reflectance spectrum of polypyrrole dodecylbenzenesulfonate appears to best follow the Drude model while portions of the spectra obtained on the other polymer films are more difficult to fit. Typical values for the plasma resonance range between $1 - 4 \times 10^{15}$ s^{-1}, while values for the carrier scattering times were on the order of 10^{-15} s.

INTRODUCTION

Polypyrrole

The considerable interest in the conducting polymer polypyrrole stems from its high conductivity (σ_{dc} = 100 mho/cm), ease of preparation and environmental stability of its doped forms. Polypyrrole, which can be synthesized by either chemical[2] or electrochemical techniques,[3] is formed by the simultaneous oxidation and polymerization of pyrrole monomer. The structure of the polymer formed by such methods contains a cationic backbone of pyrrole monomer units linked in a regular fashion through the alpha carbon atoms.[4] The positive charge of the polymer is compensated by the inclusion of dopant anions. Thus, the as-synthesized polypyrrole can be viewed (Fig. 1) as a molecular composite of negatively charged dopant ions and positively charged polymer backbone.
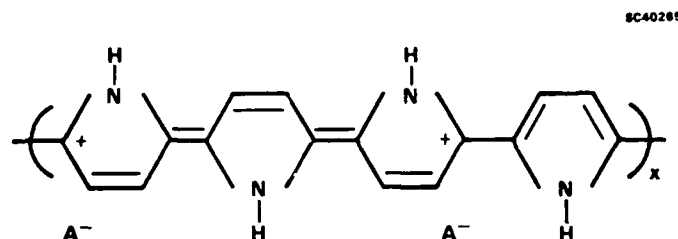
Fig. 1 Idealized structure of polypyrrole.

The mode of electrical conduction in polypyrrole and conducting polymers in general is still an issue. The most widely accepted view of electron transfer in conducting polymers invokes the idea of a complex process of electron transport along individual chains modulated by hopping from one closely associated polymer chain to another. This notion suggests that the transport properties, that is carrier mobility, carrier lifetime and carrier density, of the conducting polymer should be influenced by the arrangement of the individual polymer chains and their associated dopant ions within the polymer structure. For example, the electrical properties of a fully ordered polymer as depicted in Fig. 2 should be quite different than those of a randomly oriented polymer.

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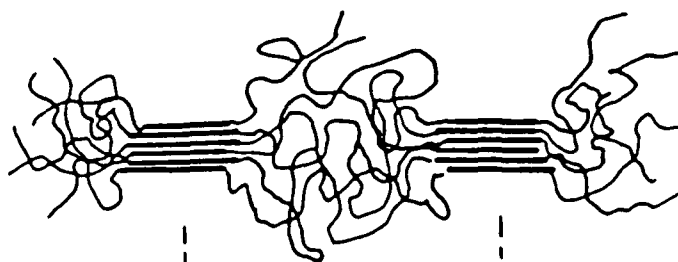
Fig. 2 Schematic drawing of an ordered and random polymer structure.

Previous work[5] has established that the morphology and conductivity of polypyrrole is largely influenced by the synthesis conditions and incorporated dopant ion. These results suggest that the transport properties of polypyrrole are also influenced by the polymer morphology. Accordingly, the work carried out under the present program addresses the issue of evaluating the transport properties of conducting polymers. That is, how are the fundamental electrical properties such as carrier density, carrier scattering time, carrier mobility and complex dielectric constants related to the polymer synthesis conditions and/or polymer morphology?

The bulk conductivity in semiconductive materials is observed to be a function of both the number of charge carriers and the mobility of the carriers:

$$\sigma = Ne\mu \quad . \tag{1}$$

Here, N represents the carrier density in cm^{-3}, e is the electronic charge and μ is the mobility in cm^2/V-s. Measuring carrier mobility in conducting polymers is problematical. The standard technique for determining both N and μ is to measure the dc electrical conductivity and the Hall effect using the well known Van der Pauw technique. In the case of materials which are microscopically one dimensional in nature, the experimental access to the Hall coefficient is not straightforward and interpretation of the data is suspect. Alternative methods for the determination of the transport properties of conducting polymers are required.

The electronic transport properties of semiconductors can be obtained by analysis of optical spectroscopic data of the material. Such techniques are particularly attractive for conducting polymers because they avoid the difficulties associated with making ohmic

contacts to the material and are nondestructive. The relation between the optical proper-
ties of semiconductive materials such as reflectance and transmission to plasma frequency
and dielectric constants is well established and methods to extract these constants from the
optical and infrared spectra have been developed.[6] It is the purpose of this program to
spectroscopically characterize electrically conducting derivatives of polypyrrole and from
these data attempt to derive electrical transport properties such as carrier mobility,
density and scattering time. The results of these studies will present a clearer picture of
the role of free carriers upon the absorption mechanisms of conductive polymers and
provide critical data relevant to the use of these materials.

EXPERIMENTAL

Materials Synthesis: Polypyrrole Films

Pyrrole monomer (Aldrich) was distilled under nitrogen and stored in a closed container in a refrigerator. All solvents were high purity reagents that were commercially obtained. Electrodepositions were performed using a PAR model 173 Potentiostat/ Galvanostat equipped with a PAR model 179 coulombmeter. Standard deposition conditions for producing films of polypyrrole are presented in Table 1.

Table 1

Deposition Conditions for Polypyrrole Film Synthesis

Solvent	Electrolyte	Current Density (mA/cm^2)	Conductivity $(\Omega^{-1} \cdot cm^{-1})$
Acetonitrile	Tetraethylammonium benzenesulfonate (0.15M)	0.761	90
Acetonitrile	Tetraethylammonium tosylate (0.15M)	~1	77
Acetonitrile	Tetraethylammonium xylenesulfonate (0.15M)	0.75	35
Water	Dodecylbenzene sulfonic acid (0.1M)	4.5	30
Water	Sodium dodecylsulfate (0.1M)	1.8	17
Acetonitrile	Tetraethylammonium biphenylsulfonate	0.65	2

The thick, freestanding polypyrrole films were deposited from a two or three electrode cell. The working electrode was either a 28 cm^2 gold-plated copper sheet (masked on the edges and back), a rectangular sheet of conducting ITO glass or a square of pyrolytic graphite. The counter electrode was either a sheet of pyrolytic graphite, a sheet of gold-plated nickel or a cylindrical platinum mesh electrode. The reference electrode, if used, was either SCE for aqueous depositions or a platinum wire for deposition from acetonitrile. Films were deposited at current densities of 0.7 to 4.5 ma/cm^2 at constant current. The films were deposited until charge equivalent to 20 - 25 coulombs/cm^2 was passed. Deposition solutions were approximately 0.1M both in pyrrole and supporting electrolyte. No precautions were taken to exclude oxygen from the cells. The films were removed from

the electrodes and rinsed thoroughly with water or acetonitrile depending upon which solvent was used. The films were dried at ambient temperature and stored in the refrigerator. Several of the films were contributed by Dr. Len Buckley of the Naval Air Development Center in Warminster, PA. Electrolytes were obtained commercially (Aldrich or Alfa). DC conductivities were determined with four point probe apparatus (Alessi Industries). Infrared spectra were recorded from 2.5 to 25 microns using a Nicolet MX-1 FT-IR spectrometer in conjunction with a diffuse reflectance sampler. Near IR reflectance (800 nm to 2.5 microns) measurements were obtained on a Perkin-Elmer model 330 optical spectrometer.

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RESULTS AND DISCUSSION

Optical Characterization: Infrared Reflectance Spectra of Polypyrrole Films

Reflectance spectra at room temperature were obtained on smooth, freestanding, thick films of doped polypyrrole in the spectral region of 0.8 to 25 microns. These spectra were obtained in the diffuse reflectance mode to minimize problems associated with sample alignment in the infrared beam and detection of reflected light. Displayed in Figs. 3 to 7 are the infrared reflectance spectra of the polymer films that were prepared.

As can be seen from these figures, all of the reflectance curves exhibit skeletal stretching modes of the pyrrole rings of the polymer at about 6.5 microns. Additionally, dopant ion absorptions occur at about 8.3 and 9.7 microns.

In general, the spectra exhibit increasing reflectance with increasing wavelength. For example, Fig. 4 displays the reflectance spectrum of a film of polypyrrole benzenesulfonate, $\sigma=90$ mho/cm. As can be seen from this figure the reflectivity increases from about 0.3 at 2.5 microns and appears to level off at 0.57 at 25 microns. The magnitude of the far IR-reflectance is related to the dc conductivity of the polymer films. For instance, the reflectance of a film of polypyrrole biphenylsulfonate, $\sigma = 2$ mho/cm, at 25 microns is about 0.27 which compares to the value of 0.57 mentioned above for the more highly conducting benzenesulfonate doped film.

Infrared Transmission Spectra of Polypyrrole Powders

Transmission spectra at room temperature were obtained on doped polypyrrole powders dispersed in potassium bromide in the spectral region of 2.5 to 25 microns (4000 to 400 cm^{-1}). Displayed in Figs. 8 to 11 are representative transmission spectra of the conducting polymers. Figure 8 shows the IR absorption of a thin pellet of polypyrrole ethylbenzenesulfonate ($\sigma = 52$ mho/cm). This spectrum exhibits bands characteristic of a pyrrole aromatic ring confirming the presence of pyrrole units in the polymer. The skeletal stretching of the pyrrole rings of the polymer is found at 1500 cm^{-1}, the C-H out of plane bending is at 775 cm^{-1} and the ring breathing occurs at 920 cm^{-1}. The peaks at 1200 cm^{-1} and 1030 cm^{-1} are assigned to the ethylbenzenesulfonate anion since these bands are observed in the spectrum of ethylbenzenesulfonic acid. The transmission spectra of polypyrrole tosylate and polypyrrole dodecylbenzenesulfonate are qualitatively similar and are displayed in Figs. 10 and 11, respectively.

7

Fig. 3   Infrared reflectance spectrum of thick film of
polypyrrole biphenylsulfonate.

Fig. 4   Infrared reflectance spectrum of thick film of
polypyrrole benzenesulfonate.
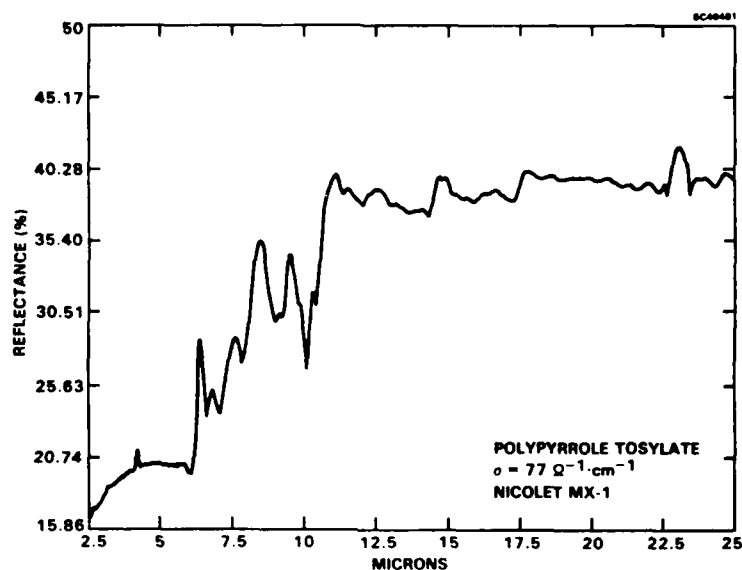
Fig. 5   Infrared reflectance spectrum of thick film of
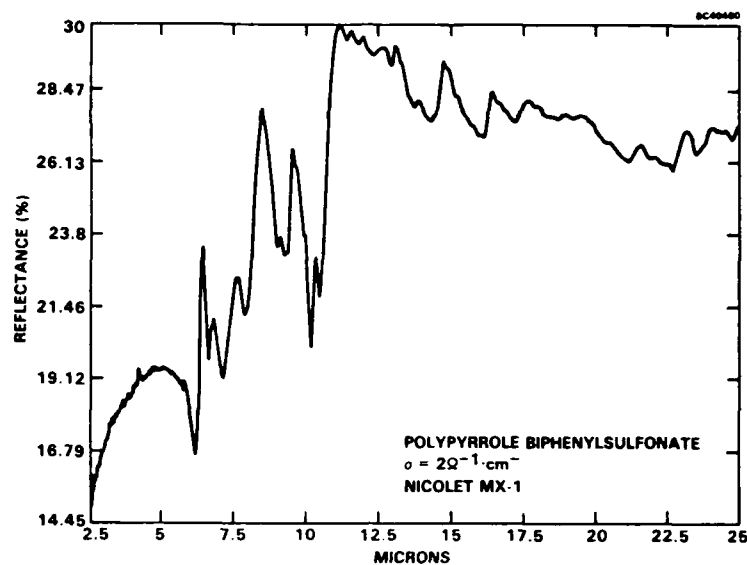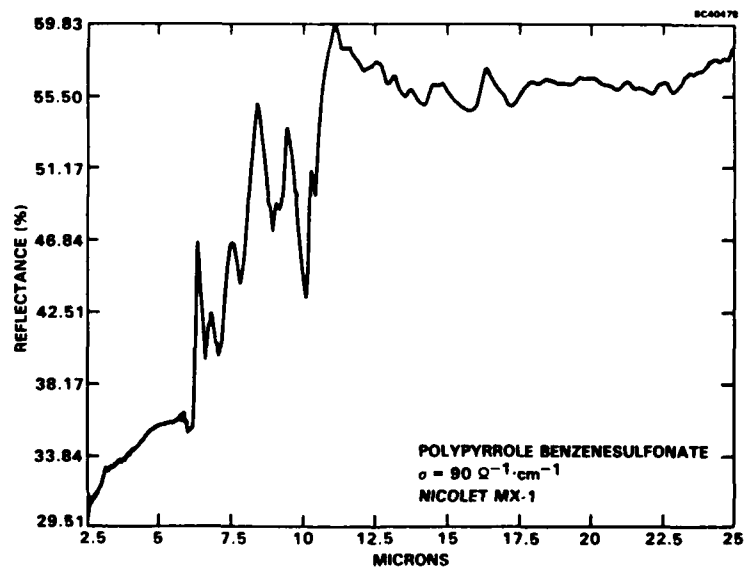polypyrrole tolsylate.
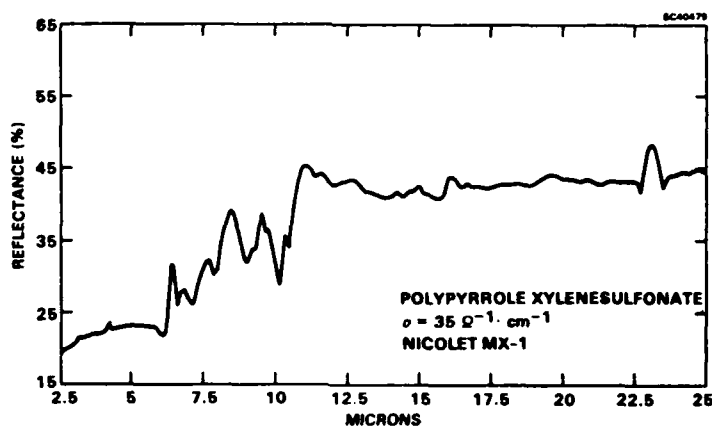
Fig. 6   Infrared reflectance spectrum of thick film of
polypyrrole xylenesulfonate.
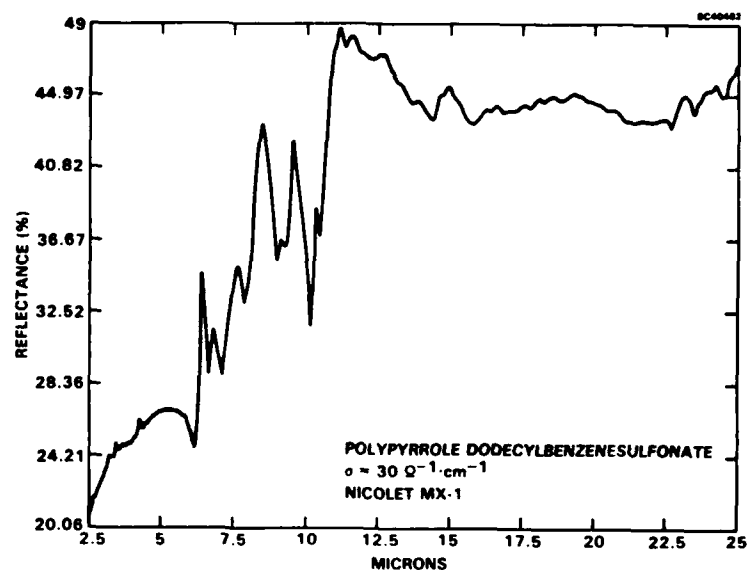
Fig. 7   Infrared reflectance spectrum of thick film of polypyrrole dodecylbenzenesulfonate.
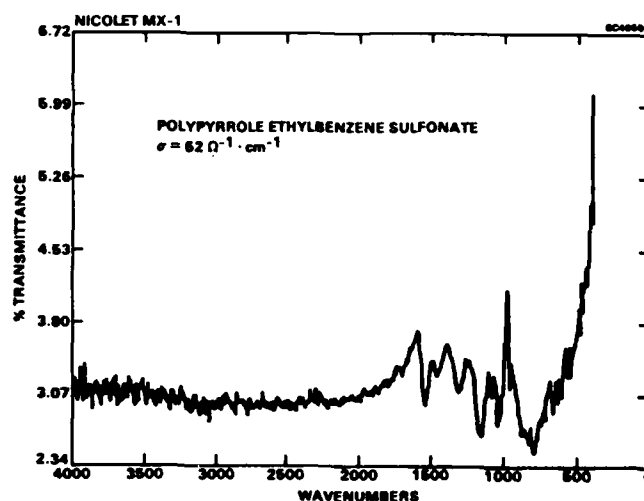
Fig. 8   Infrared transmission spectrum of polypyrrole ethylbenzene sulfonate dispersed in KBr.

NICOLET MX-1

POLYPYRROLE ETHYLBENZENE SULFONATE
AMMONIA COMPENSATED
$\sigma = 0.07\ \Omega^{-1} \cdot cm^{-1}$

% TRANSMITTANCE

WAVENUMBERS

Fig. 9 Infrared transmission spectrum of polypyrrole
ethylbenzenesulfonate compensated in KBr.

POLYPYRROLE TOSYLATE
$\sigma = 36\ \Omega^{-1} \cdot cm^{-1}$

% TRANSMITTANCE

WAVENUMBERS

Fig. 10 Infrared transmission spectrum of polypyrrole
tosylate dispersed in KBr.
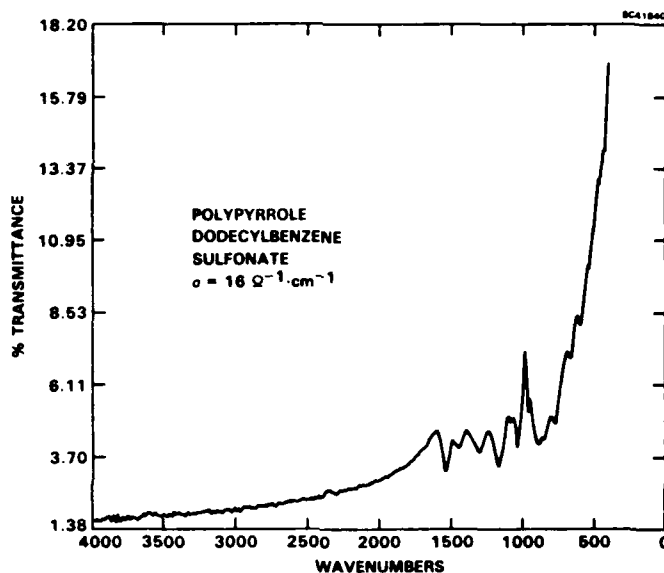
Fig. 11 Infrared transmission spectrum of polypyrrole dodecylbenzenesulfonate dispersed in KBr.

The origin of the broad absorption band present in these spectra at frequencies above 1600 cm^{-1} is not known with certainty but is characteristic of doped polypyrrole materials. This band is associated with the number of carriers, however, because the intensity is proportional to the conductivity of the polymer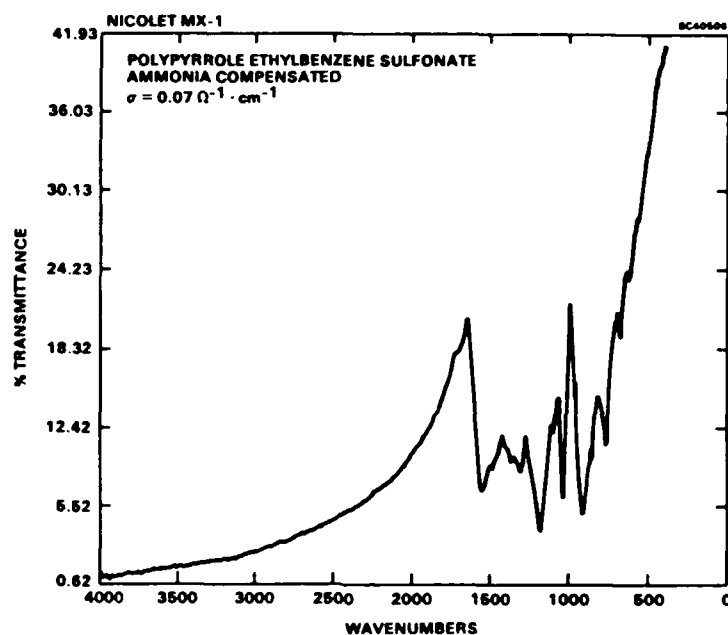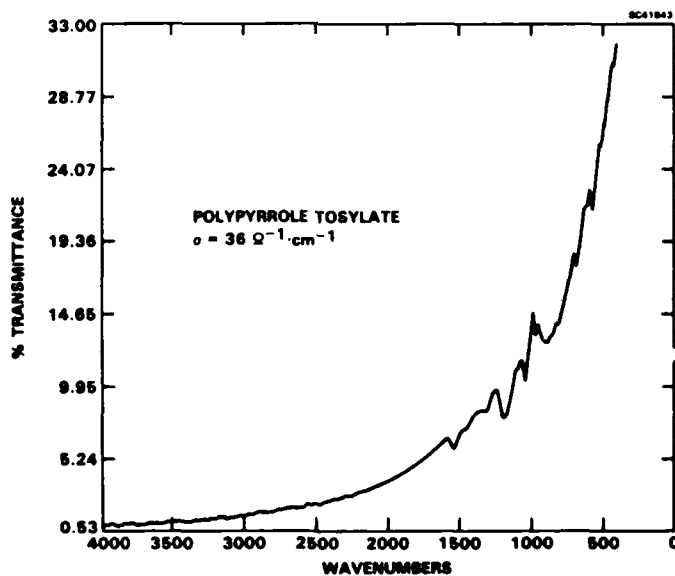 sample. For example, the IR transmission of a sample of polypyrrole ethylbenzenesulfonate (σ = 52 mho/cm) in KBr at 1750 cm^{-1} is approximately 3.1% while the transmission of a similar sample of ammonia compensated polypyrrole ethylbenzenesulfonate (σ = 0.07 mho/cm) at the same wavelength (spectrum shown in Fig. 10) is approximately 16%. The broad nature and energy may be understood in terms of the energy-band diagram shown in Fig. 12, which has been proposed for the electronic structure of doped polypyrrole.[1] As can be seen from this diagram, the neutral polymer is a relatively large band-gap material that should be transparent in the near IR. As the polymer is doped, however, mid-gap states are introduced which can result in optical absorptions in the UV-visible and near-IR spectral regions. In particular, transitions from the valence band to the first mid-gap state have been proposed[7] to occur at the wavelength of the absorption edge observed in the IR spectra of the polypyrrole materials.

SC40508

CB

Eg

VB

(a)

CB

ω_2

ω_1 ω_3

VB

(b)
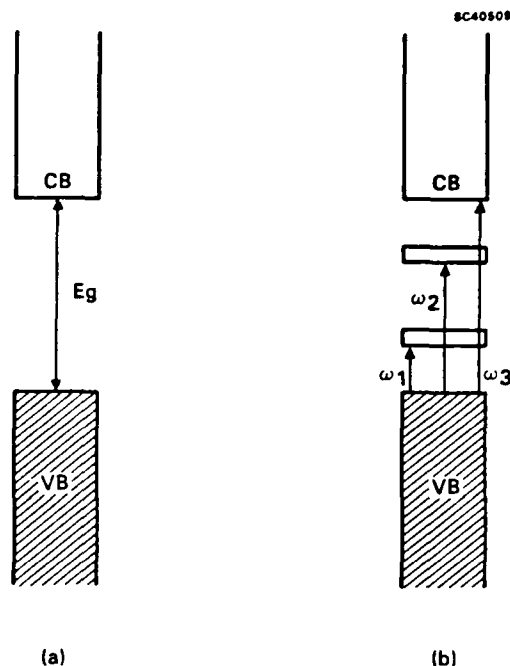
Fig. 12 Proposed energy level diagram for doped polypyrrole.

Spectral Analysis

The Drude model for the dielectric function of an electron gas may be expressed by the following equation:

$$\epsilon(\omega) = \epsilon_{core} - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \ . \tag{2}$$

Here, ϵ_{core} is the dielectric constant at high frequency arising from the core polarizability, ω_p is the plasma frequency and γ is the band width. The infrared reflectance data may be fit to the following equations:

$$R = \frac{1 + |\epsilon| - \sqrt{2(|\epsilon| + \epsilon_1)}}{1 + |\epsilon| + \sqrt{2(|\epsilon| + \epsilon_1)}} \tag{3a}$$

$$|\epsilon| = \sqrt{\epsilon_1^2 + \epsilon_2^2} \tag{3b}$$

$$\epsilon_1 = \epsilon_{core} - \frac{\omega_p^2}{\omega^2 + \gamma^2} \tag{3c}$$

$$\epsilon_2 = \frac{\gamma \omega_p^2}{\omega^3 + \gamma^2 \omega} , \tag{3d}$$

where ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric function. The plasma frequency can be related to the carrier density per unit volume, N_c, and the optical effective mass of the carriers, m^*, by Eq. (4).

$$N = \frac{\omega_p^2 m^*}{4\pi e^2} . \tag{4}$$

Employing this type of spectral analysis, Tanaka et al[8] were able to deduce values for the plasma resonance in a related conducting polymer, poly-3-methylthiophene. The data presented by those workers suggested a value for the carrier density to be on the order of 10^{21} cm^{-3} and a plasma frequency of 670 nm. The scattering time suggested by this analysis was on the order of 10^{-15} s. Tanaka similarly analyzed the reflectance spectrum of polypyrrole perchlorate and derived comparable values for the carrier density, plasma frequency, and carrier lifetime.[9] The general values for these quantities are quite unusual. The high energy plasma resonance and very short lifetimes are particulaly notable. As these values were unexpected we set out to verify these results and more closely examine the dependence of the transport properties and complex dielectric constants upon the polymer synthesis conditions, polymer bulk conductivity and incorporated dopant ion.

Parametric values for the band width, gamma and the plasma resonance frequency, ω_p, can be fit to the observed reflectance spectrum using Eq. (3). In all cases, however, the simple Drude model for the dielectric function underestimated the magnitude of the infrared reflectivity in the near infrared spectral region between 2.5 and 10 microns. This observation suggested that additional absorption mechanisms besides the free carrier absorption contribute to the dielectric function in this spectral region or that the free carrier absorption is nonexistent at wavelengths less than 10 microns and some other absorption mechanism is operational. The generalized form of the dielectric function used to explain free carrier absorption is as follows:

$$\epsilon(\omega) = \epsilon_{core} + \sum_{j=1}^{N} \frac{S_j \omega_j^2}{\omega_j^2 - \omega^2 - i\gamma_j \omega} - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad , \tag{5}$$

where, as before, ϵ_{core} is the high frequency lattice dielectric constant, the second term is a summation over lattice modes represented by "N" oscillators with strength S_j, a resonant frequency ω_j and damping constant γ_j. The third term represents the free carrier part of the dielectric constant as before. In the present case, the reflectance spectra were fit using a model for the dielectric function that contains the Drude expression and one additional oscillator term. This oscillator term accounts for absorption that arises from electronic transitions between the valence band and the lowest bipolaronic energy state[7] as indicated in Fig. 12.

Thus, the real and imaginary parts of the complex dielectric function can be written as follows:

$$\epsilon_1 = \epsilon_{core} - \frac{\omega_p^2}{\omega^2 + \gamma^2} + \frac{S_1 \omega_1^2 (\omega_1^2 - \omega^2)}{(\omega_1^2 - \omega^2)^2 + \gamma_1^2 \omega^2} \tag{6}$$

$$\epsilon_2 = \frac{\gamma \omega_p^2}{\omega^3 - \gamma^2 \omega} + \frac{S_1 \omega_1^2 \omega}{(\omega_1^2 - \omega^2) + \gamma_1 \omega^2} \tag{7}$$

and the reflectance can be calculated as before. Set out in Table 2 are the results of fitting the observed reflectance spectra displayed in Figs. 3 to 7 to the dielectric function presented above.

Examination of the data presented in the table indicates that the free carrier plasma frequency in these materials occurs at surprisingly high energy. In all of the poly-pyrrole films examined in this work, the best spectral fits to the Drude model occurred when the plasma resonance frequency was adjusted between $1 - 4 \times 10^{15}$ s^{-1}. The fitting procedure also required that the bandwidth assume values between $1 - 3 \times 10^{-16}$ s^{-1} while the value of the core dielectric constant varied between 2.4 and 2.7. The frequency and bandwidth of the second oscillator term can also be characterized by resonance energies,
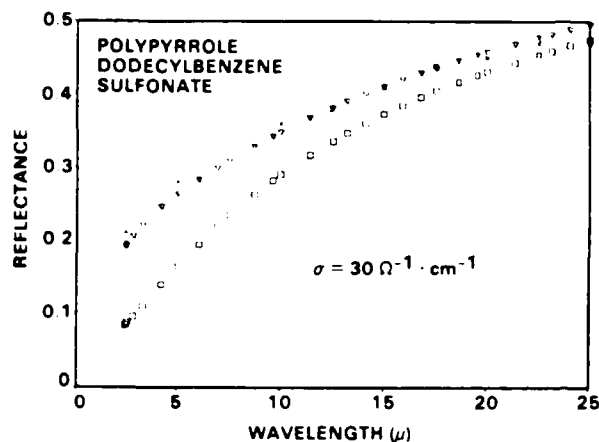
Table 2

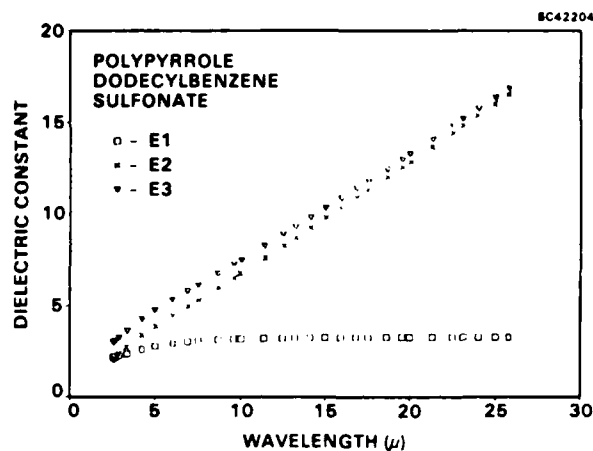## Optical Parameters of Doped Polypyrrole Films at 300K

Dopant Anion	Plasma Frequency (s^{-1})	Relaxation Time (s)	ϵ_{core}	Damping Constant (γ_i, s^{-1})	Oscillator Frequency (ω_i, s^{-1})	Oscillator Strength
Benzene Sulfonate	3.76×10^{15}	1.8×10^{-16}	2.7	3×10^{14}	9.6×10^{-13}	0.98
Tosylate	2.07×10^{15}	1.6×10^{-16}	2.5	1.5×10^{14}	9.6×10^{-13}	0.95
Xylenesulfonate	2.82×10^{15}	1.5×10^{-16}	2.7	1.5×10^{14}	9.6×10^{-13}	0.95
Dodecylbenzenesulfonate	2.63×10^{15}	1.71×10^{-16}	2.5	1.5×10^{14}	9.6×10^{-13}	0.95
Biphenylsulfonate	1.12×10^{15}	2.79×10^{-16}	2.4	3×10^{14}	9.6×10^{-13}	1.36

bandwidths and oscillator strengths. Spectral fits were obtained by using a typical value for the resonant frequency at 9.6×10^{-13} s^{-1} while parameters for the bandwidth were found between $1.5 - 3 \times 10^{14}$ s^{-1}.

Displayed in Fig. 13a are the results of fitting the observed reflectance spectrum of polypyrrole dodecylbenzenesulfonate to the calculated spectrum. In this figure, the cross shaped data points correspond to points taken from the observed spectrum (phonons have been omitted) while the rectangular and triangular data points are the calculated points using the simple Drude model (Eq. (3)) and the modified dielectric function respectively (Eqs. (6) and (7)). As can be seen from this figure, an excellent fit to the observed spectrum was achieved using the two oscillator model for the dielectric function. This model adequately predicts both the near- and far-infrared reflectivity. In contrast, the simple Drude model for the dielectric function only appears to accurately predict the reflectance at far-infrared wavelengths and does not adequately predict the reflectivity and dielectric constants at the higher frequencies. This indicates that the dominant absorption mechanism in the far-infrared region and beyond to the millimeter and microwave region is due to the free carriers. In contrast, the near-infrared absorption appears to be dominated by electronic transitions. Displayed in Figs. 13a - 17a are the calculated reflectance spectra of the polymer films that were characterized.

SC42204

POLYPYRROLE
DODECYLBENZENE
SULFONATE

$\sigma = 30 \, \Omega^{-1} \cdot cm^{-1}$

POLYPYRROLE
DODECYLBENZENE
SULFONATE

□ – E1
× – E2
▼ – E3

(a)

(b)

Fig. 13   Calculated reflectance spec-
trum for polypyrrole dodecyl-
benzenesulfonate.

Fig. 13   Calculated dielectric con-
stants for polypyrrole dode-
cylbenzenesulfonate.

SC42203

POLYPYRROLE
TOSYLATE

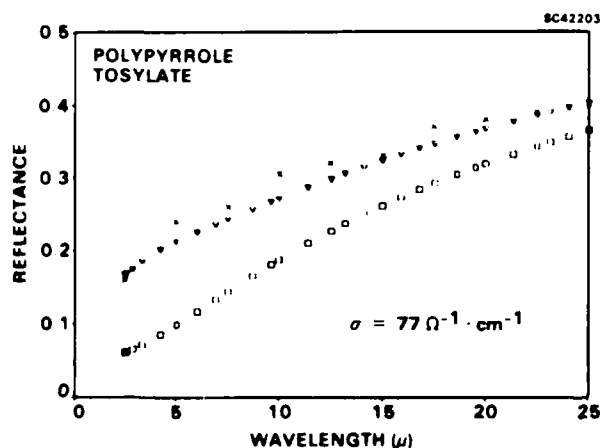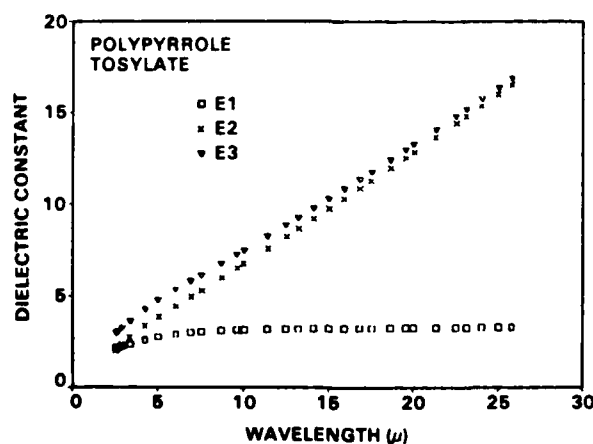$\sigma = 77 \, \Omega^{-1} \cdot cm^{-1}$

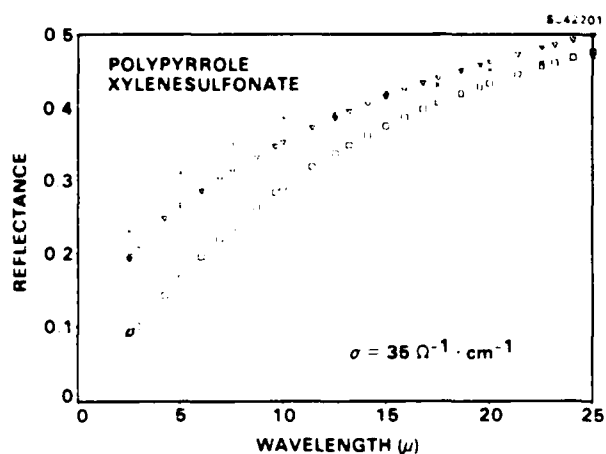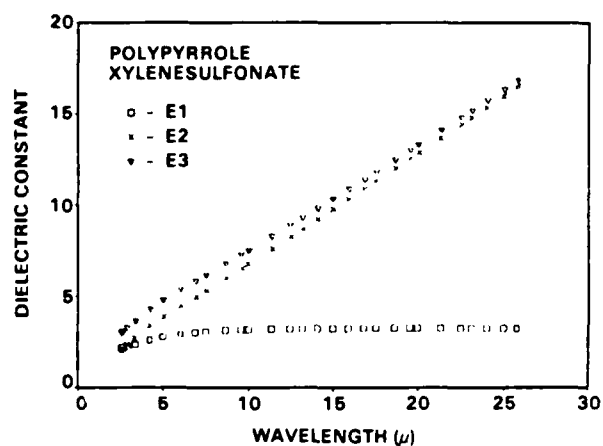POLYPYRROLE
TOSYLATE

□ E1
× E2
▼ E3

(a)

(b)

Fig. 14   Calculated reflectance spec-
trum for polypyrrole
tosylate.

Fig. 14   Calculated dielectric con-
stants for polypyrrole
tosylate.

S-42201

POLYPYRROLE
XYLENESULFONATE

REFLECTANCE

$\sigma = 35\ \Omega^{-1} \cdot cm^{-1}$

WAVELENGTH (μ)

(a)

Fig. 15   Calculated reflectance spec-
trum for polypyrrole
xylenesulfonate.

POLYPYRROLE
XYLENESULFONATE

□ – E1
× – E2
▼ – E3

DIELECTRIC CONSTANT

WAVELENGTH (μ)

(b)

Fig. 15   Calculated dielectric con-
stants for polypyrrole
xylenesulfonate.

SC42250

POLYPYRROLE
BENZENESULFONATE

REFLECTANCE

$\sigma = 90\ \Omega^{-1} \cdot cm^{-1}$

WAVELENGTH (μ)

(a)

Fig. 16   Calculated reflectance spec-
trum for polypyrrole
benzene sulfonate.

SC42252

POLYPYRROLE
BENZENESULFONATE

□ E1
× E2
▼ E3

DIELECTRIC CONTANT

WAVELENGTH (μ)

(b)

Fig. 16   Calculated dielectric con-
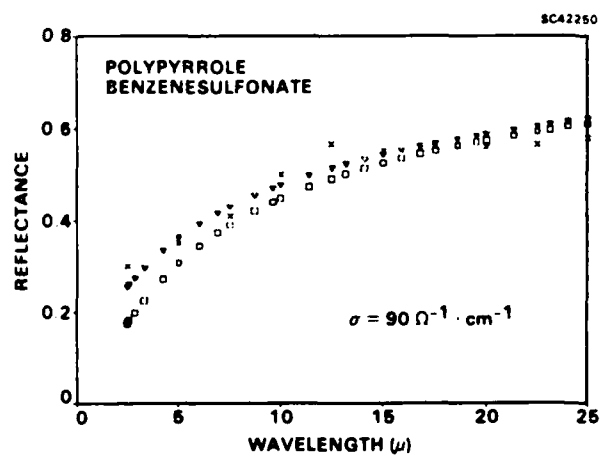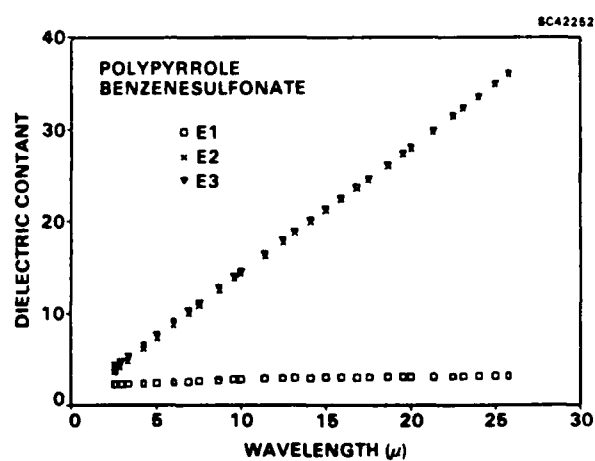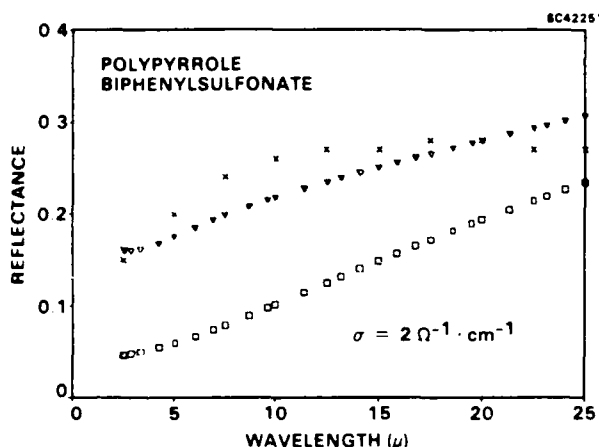stants for polypyrrole
benzene sulfonate.
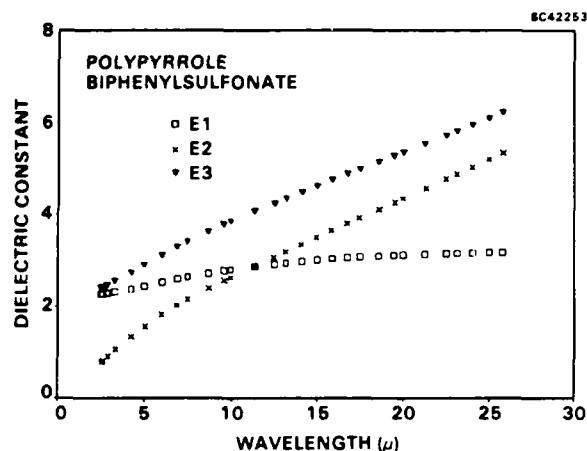
(a)

Fig. 17   Calculated reflectance spec-
trum for polypyrrole
biphenylsulfonate.

(b)

Fig. 17   Calculated dielectric con-
stants for polypyrrole
biphenylsulfonate.

The complex dielectric constants as expressed by Eq. (6) and Eq. (7) can be evaluated at selected frequencies in the infrared spectral region. Figures 13b - 17b display the frequency dependence of the real and imaginary parts of the complex dielectric constants along with the calculated and observed reflectance spectra. As seen from these figures, the real part of the dielectric constant remains essentially consta.it at infrared frequencies while the imaginary part of the dielectric constant typically increases by a factor of 5-6 in the spectral region of 2.5 to 25 microns. The complex dielectric constant is therefore largely determined by the magnitude of the imaginary part of the dielectric constant. The general magnitude of the dielectric constants appeared to track the conductivity levels of the polymer films. For example, the magnitude of the complex dielectric constants evaluated at 25 microns ranged from a high value of 31.5 for the most highly conducting benzenesulfonate doped film to 6.1 for least conducting biphenylsulfonate doped film.

The imaginary part of the dielectric constant can be related to the conductivity by Eq. (8):

$$\epsilon'' = \frac{\sigma}{\omega \epsilon_0} \tag{8}$$

where σ is the conductivity, ω is the angular frequency and ϵ_0 is the permittivity of free space. It should be noted that the values for the conductivity calculated via Eq. (8), are two

to four times higher than the observed dc conductivities. This observation may suggest that additional loss mechanisms exist at nonzero frequencies in these materials or that a form of internal resistance present in the polymer reduces the bulk conductivity levels of the conductive polymer. This added resistivity has been attributed to electron hopping resistance between polymer chains. Reduction of this interchain resistance, by alignment of the polymer chains, for instance, potentially, could increase the conductivity levels of the polymers.

The values assigned to plasma resonance frequency and carrier scattering time can be used to respectively calculate the carrier density, N, and the carrier mobility μ via Eqs. (3) and (9) if the carrier mass is assumed to be equal to the mass of the electron.

$$\mu = \frac{e\tau}{m^\star} \quad . \tag{9}$$

Using this assumption, values for the carrier mobility and carrier density have been calculated and the results are tabulated in Table 3.

Table 3

Calculated Values of the Carrier Density, Carrier Mobility and
Optical Conductivity of Polypyrrole Films (T = 300K)

Dopant Anion	Carrier Density (cm^{-3})	Carrier Mobility $(cm^2/V \cdot s)$	Optical Conductivity $(\Omega^{-1} \cdot cm^{-1})$
Benzenesulfonate	3×10^{20}	0.32	18
Tosylate	1×10^{20}	0.28	5
Xylenesulfonate	2×10^{20}	0.26	9
Dodecylbenzenesulfonate	2×10^{20}	0.30	8
Biphenylsulfonate	3×10^{19}	0.49	32

(a) Calculations based upon carrier mass equal to the mass of the electron.

As an example, calculation of the carrier density based upon the plasma resonance of 11,000 cm^{-1} assigned to polypyrrole tosylate yields a value of 1×10^{20} cm^{-3}. This value corresponds to ca. 0.3% of the total π-electrons (4×10^{22} cm^{-3}) which is estimated from the density of the film ($\rho = 1.41 g/cm^3$; calculation based upon 6 π electrons/pyrrole unit and

dopant mole fraction of 0.43). Further, this value corresponds to a dopant activation very much lower than the observed dopant concentration of one anion per 3-4 monomer units. This may suggest that only a few of the holes in the valence band contribute to the transport properties of the conductive polymer. It should be noted, however, that the carrier mass is in general not equal to the mass of the electron. A quantitative determination of the carrier mass in these materials would require separate experiments such as cyclotron resonance.

Equation (9) relates the carrier scattering time to the carrier mobility and carrier effective mass. A representative value for the mobility may be calculated for polypyrrole tosylate as 0.3 cm^2/V-s, again assuming that the carrier mass is equal to the mass of the electron. The magnitude of the calculated carrier mobilities is very small and is consistent with a highly disordered defective solid. This is probably attributable to the presence of many electronic traps and interfibrillar contact resistance. For example, beta-coupling of monomer units would cause the formation of a localized electronic energy state that would behave as an electron trap. Increasing the carrier mobility by reduction of the number of electronic trap states would allow for much higher conductivity levels in the conductive polymer.

The calculation of the carrier densities and mobilities allows us now to return to Eq. (1) and compare the values of the calculated conductivities to the values measured on the polymer films. Equation (10) results from substitution of Eq. (4) for the carrier density and Eq. (8) for the carrier mobility:

$$\sigma_{dc} = \frac{\omega_p^2 \tau}{4\pi} \ . \tag{10}$$

The results of these calculations are presented in Table 3. The most striking feature of these results is the magnitude of the calculated optical conductivity. These values were typically calculated to be a factor of 2-4 lower than the measured dc conductivity levels. For example, the optical conductivity of polypyrrole tosylate was calculated to be 19 mho/cm while the measured dc conductivity was about 80 mho/cm. Several observations can be made regarding the optical conductivities and Eq. (10). The first is that the inherent conductivities of conductive polymer films can be much greater than their measured conductivity levels. This observation is based upon the concept that interparticle contact resistance within the films limits the magnitude of the observed conductivity. Equation (10)

also shows that higher conductivity levels may be realized by prolonging the carrier lifetime. As mentioned above, the short carrier lifetimes are probably the result of numerous defect trap states caused by the presence of polymer defects such as cross-links, dangling or broken bonds or oxidation sites. A reduction of the number of these trap states by improving the purity or crystallinity of the conductive polymer will ultimately result in much higher conductivity levels in the conductive polymer.

CONCLUSIONS

The transport properties of a series of conductive polymer films were evaluated by analyzing their infrared reflectance spectra in terms of a modified Drude expression for the dielectric function. This analysis yielded values for the carrier scattering times, plasma frequencies, and core dielectric constants for each polymer film. The parameters extracted from the spectral analysis were in turn used to calculate values for the complex dielectric constants, carrier densities, carrier mobilities and optical conductivities. Perhaps the most important obervation to be made from this analysis is that the electrical properties calculated from the optical parameters were in all cases in general agreement with the measured properties. The electrical transport properties at wavelengths beyond the milli-meter range are primarily due to free carriers while an optical transition involving a midgap state dominates at wavelengths shorter than the mid IR. The conclusion to be drawn from this observation is that the optical spectroscopic techniques described in this report are extremely useful for the determination of the transport properties of conducting polymers.

The indicated carrier lifetimes or mobilities suggest that the as-synthesized, doped polypyrrole materials are probably not suitable for electronic device applications. Improvements in carrier lifetimes and mobilities may be achieved through the development of improved synthesis or processing techniques.

The Drude analysis of the infrared reflectance spectra demonstrates the utility of using optical spectroscopic techniques for the approximate determination of the transport properties of conductive polymers. However, if the one considers the wide distribution of conjugation lengths that exist in most conductive polymers, then it can be appreciated that the parameters derived from this type of analysis represent bulk, average values for the transport properties. A study of the electrical properties of individual polymer chains or highly crystalline, ordered conducting polymers may reveal that these properties are quite different than the bulk properties reported here.

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